SAND2011-7848C

U.S. DEPARTMENT OF ENERGY | Nuclear Energy

Fuel Cycle Research and Development

Volatile Gas Capture Development

Tina M. Nenoff, Terry J. Garino, James L. Krumhansl, Dorina F. Sava, David Rademacher, Jeffrey Greathouse, Benjamin Cipiti, Haiqing Liu

Developments in Nuclear Waste Forms Panel Discussion
Materials for Nuclear Waste Disposal and Environmental Cleanup
MS&T 2011
Columbus, OH October 19-20, 2011

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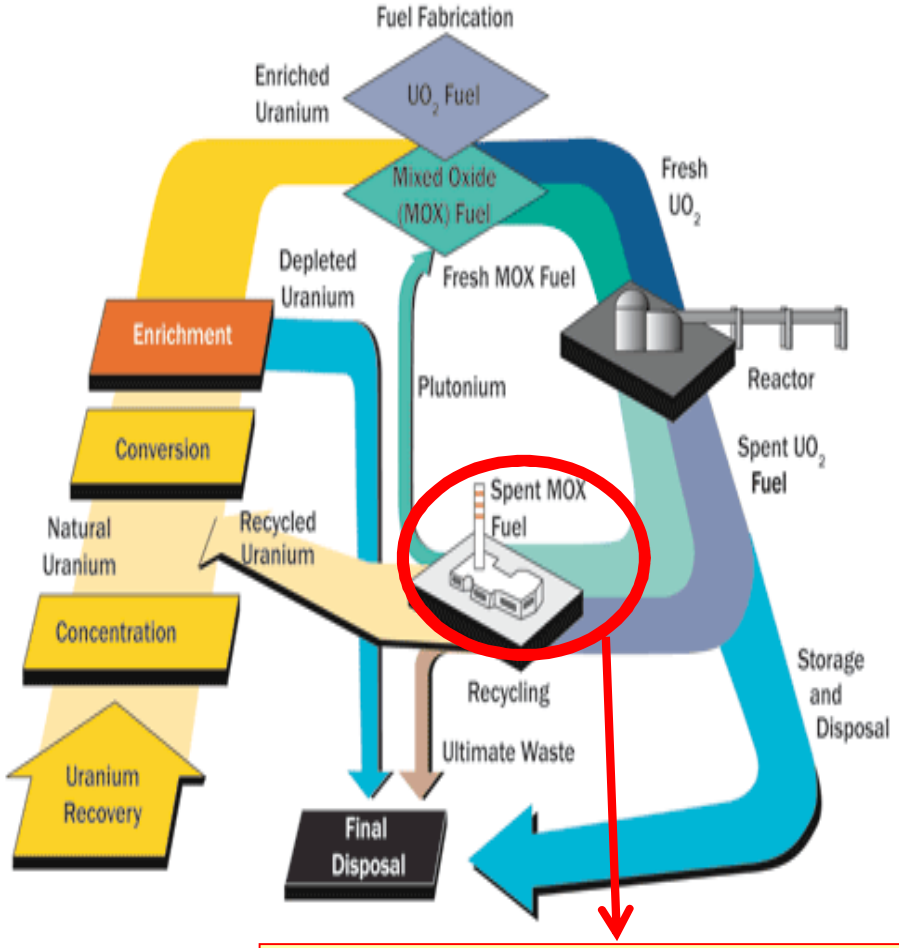
Overview – Separations & Storage

I. Nuclear Waste Legacy (EM) for USA and the world

Fukashima Daiichi Nuclear Power Plant explosion March 11, 2011: I^{129}, I^{131} volatile gas released; Cs^{135}, Cs^{137} aqueous released
(www.IAEA.org)

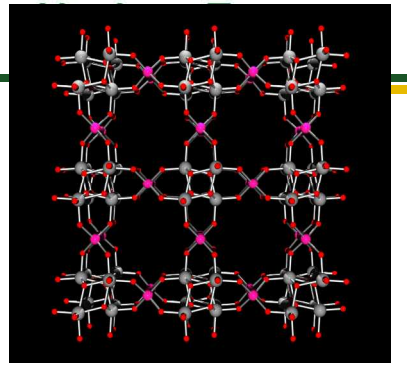
II. Nuclear Fuel Reprocessing (NE)

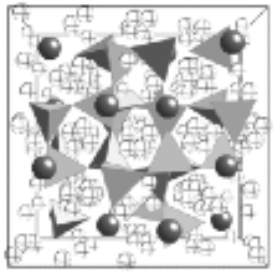


Source: U.S. Nuclear Regulatory Co

Separations of non-burnable volatile fission products and lesser actinides

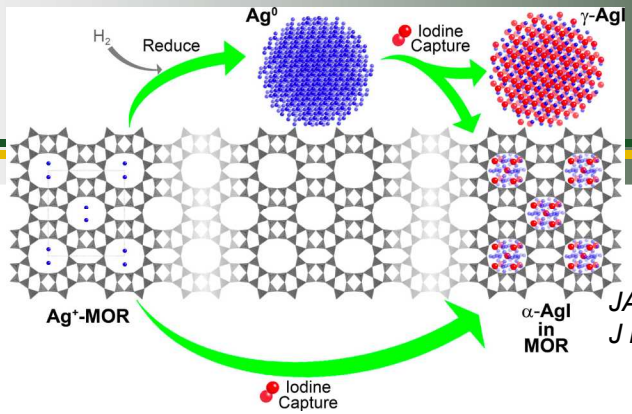
SNL Overview – Capture/Storage





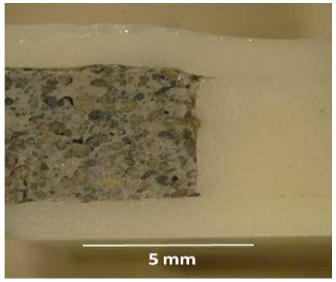
R&D100 1996
JACerS, **2009**, 92(9), 2144
JACerS, **2011**, 94(9), 3053
Solvent Extr. & Ion Exch, **2011**, submitted

CST, Cs^+ removal from water to Pollucite Waste Form



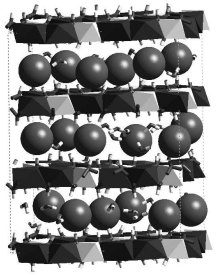
Ag-MOR
I_2(g) capture & mechanisms
JACS, **2010**, 132(26), 8897
J Phys Chem Letters, **2011**, 2, 2742

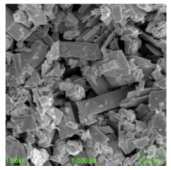
Fundamental Research to Applied to Commercial Products
Design the Separation Material To Develop the Waste Form



Universal Core-Shell Glass Waste Form Iodine & Getter
JACerS, **2011**, 94(8), 2412

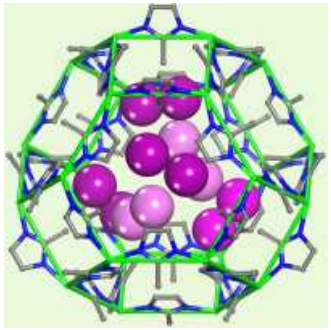
Applied Geochem, **2011**, 26, 57

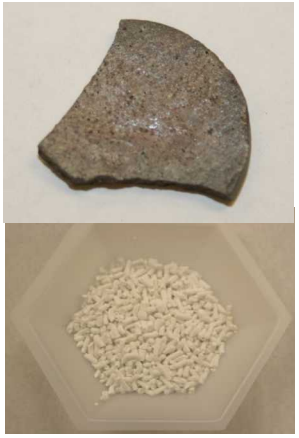


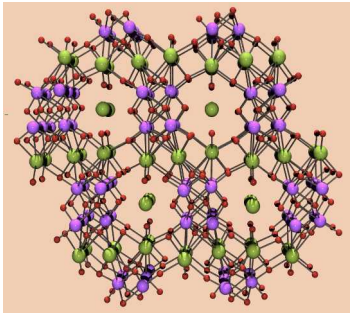


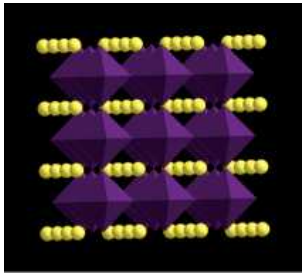
In-situ Iodine removal from water

I_2/MOF, Isolation to Waste Form
JACS, **2011**,133(32),12398
Ind. Eng. Chem. Res, **2011**, ASAP
US Patent Application, 2011









Sr getter, 1-step to Perovksite waste form
JACS, **2002**,124(3), 1704

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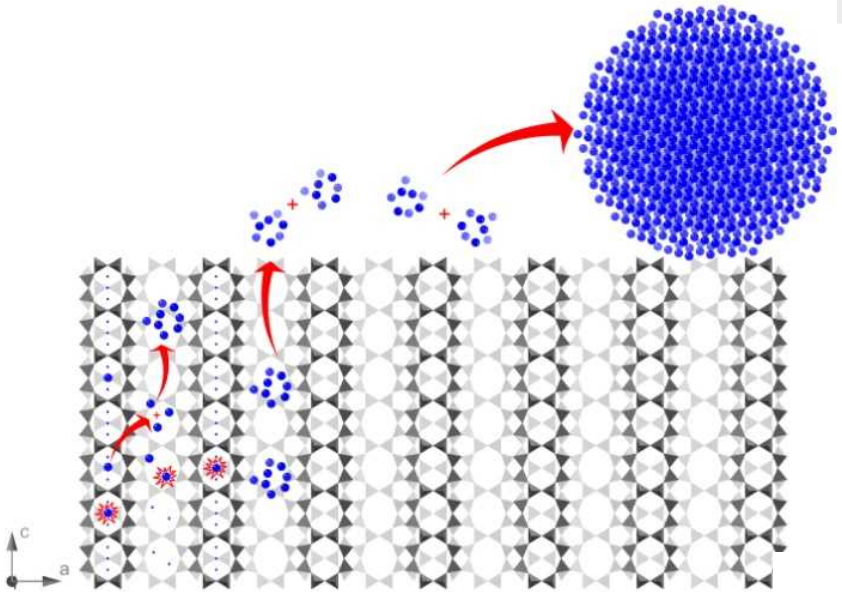
Ag-MOR zeolite for I_2 Capture and Temporary Storage

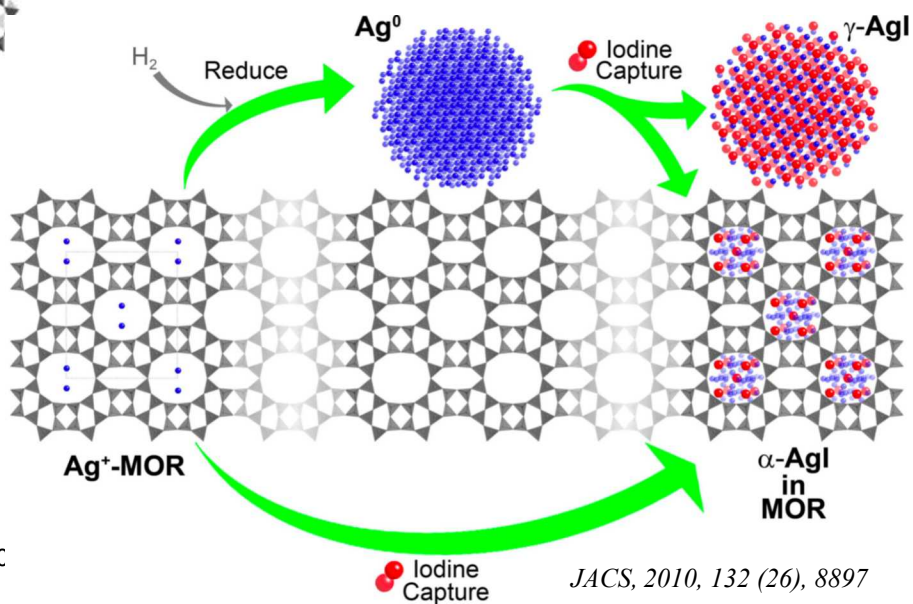


Ag^+-MOR ion reduction to Ag° clusters and migration out of pores upon nanoparticle formation

J Phys Chem Letters, 2011, 2, 2742

Ag°-MOR + I_2 yields a mixture of γ-AgI bulk surface nanoparticles and sub-nanometer α-AgI.

Ag^+-MOR + I_2 produces exclusively sub-nanometer α-AgI ("**perfect fit**", confined in pores)



JACS, 2010, 132 (26), 8897

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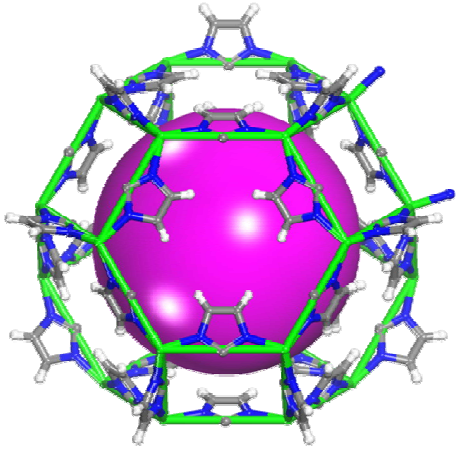
Separations Materials Studies - MOFs

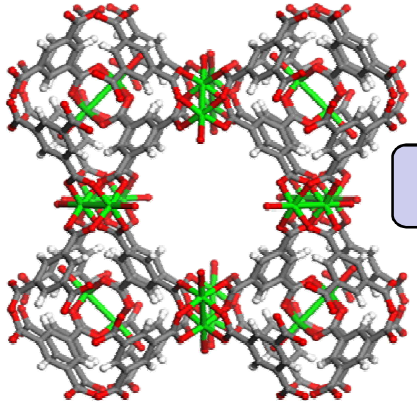
Understand the Scientific Basis for the Capture and Immobilization Technologies

Basolite Z1200, ZIF-8
Constricted Pore Opening (≈ 3.4Å)
1100 – 1600 m^2/g
Pore Volume = 0.636 cc/g
stable in Air & H_2O



I_2@ZIF-8 ~ 125 wt.% I_2

Basolite C300, HKUST-1
Open Channels, ≈ 1nm in 3D
1500-2100 m^2/g
Exposed Metal Sites of Framework



I_2@HKUST-1 ~ 150 wt.% I_2

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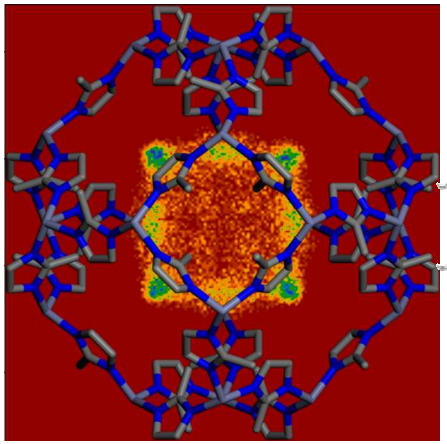
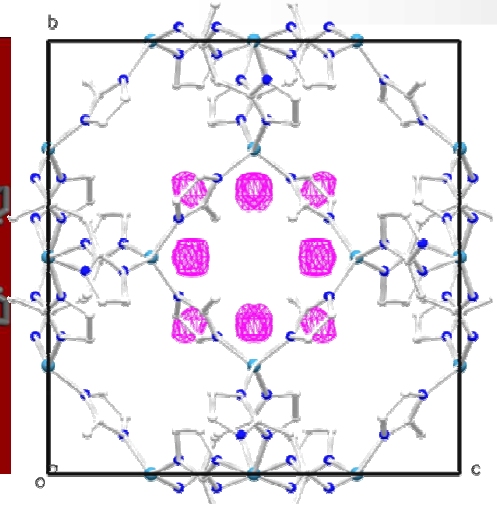
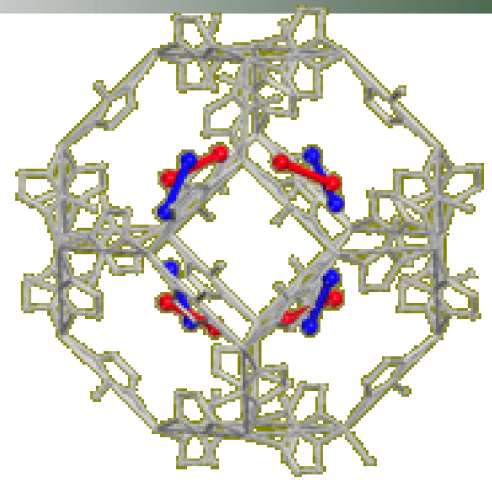
Fundamental Studies to Understand Iodine Separations and Capture



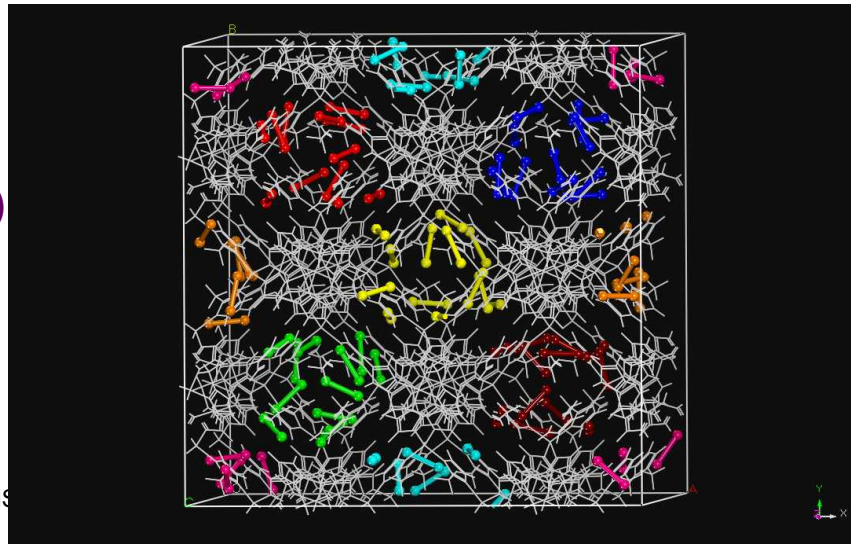




Modeling + crystallography

ZIF-8/I_2 Structure Determination

NEAMS Modeling (MD simulations) Indicate cage trapment of I_2



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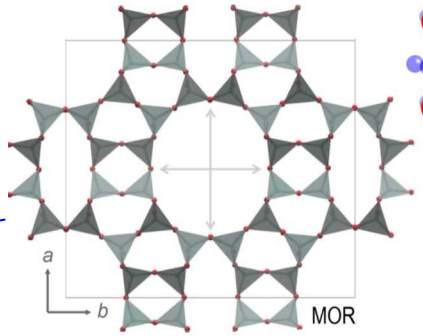
Waste Forms – Low Temperature Sintering Glass for GCM Waste Form

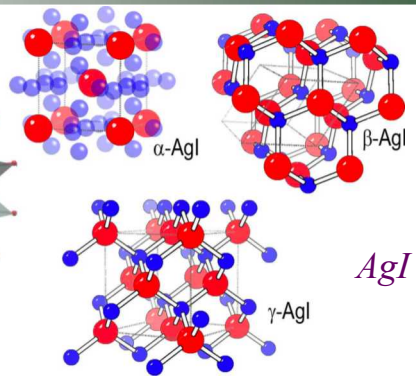
*JACerS, **2011**, 94(8), 2412*

Homogenous Glass GCM: for
AgI or AgI-MOR off-gas capture and storage

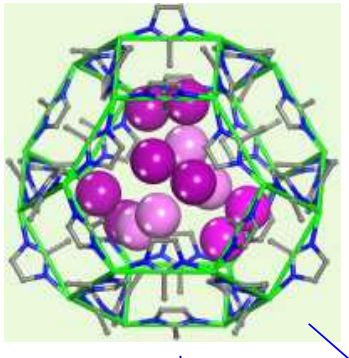
50 wt% AgI/50 wt% Glass
500°C for 3 hr

50 wt% AgI/50 wt% Glass,
500°C for 3 hr





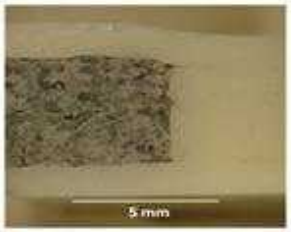
AgI mp 556°C



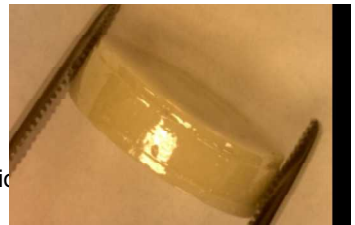
I_2/MOF, Isolation to Waste Form
*JACS, **2011**,133(32),12398*
*Ind. Eng. Chem. Res, **2011**, ASAP*
US Patent Application, 2011

Core-Shell GCM Glass Waste Forms

Glass shell, AgI/glass core, 75/25



Glass shell,
AgI-MOR/Ag/Glass core 80/20/5



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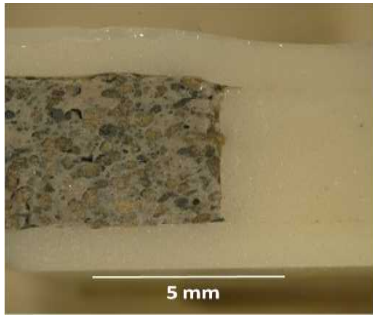
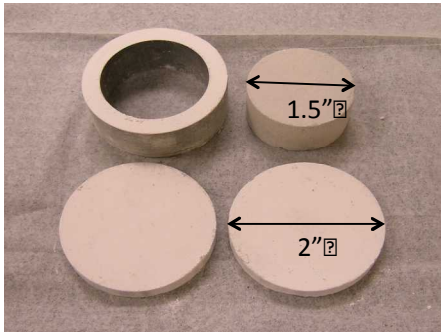
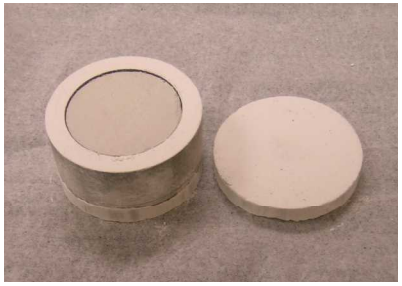
Waste Forms – Low Temperature Sintering Glass Core-Shell Scalable Composition

Universal Core-Shell Glass Waste Form Iodine & Getter







Scale-up

Proof of Concept Completed

Industrialization?: Fabrication and stockpile of core/shell components for as-needed use

Better understanding of performance in real-world conditions needed

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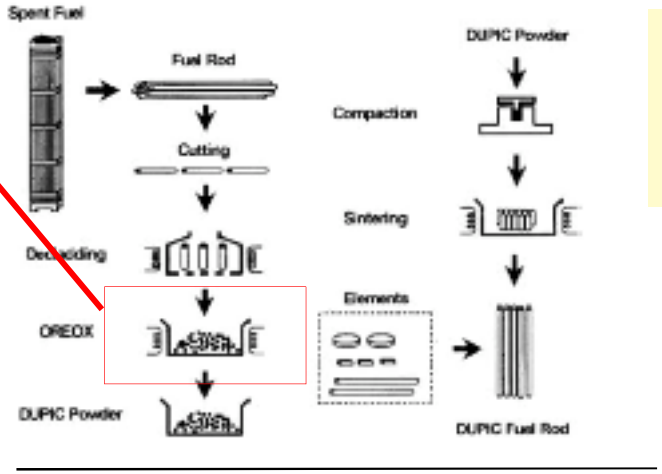
Related MOC Project: Ceramic Nanofiber Membranes

Removal of Fission Products and Poisons for Fuel Recycle:

- crushing the fuel
- performing a simplified heating process and/or hot gas extraction process (≈ 650-1500°C)
- separate out the volatile fission products (eg., Cs, Sr, Rb) and poisons (eg., Xe)
- recycle of the fuel through mixing with fresh fuel and re-sintering



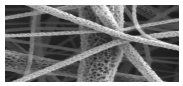
Kang, et.al., Metal.Mater. 2000, 6(6), 583

DUPIC-like Fuel Fabrication Process:

Model process system for insertion of nanofiber membrane & capture products during heating

Del Cul, et al., Advanced Head-End Processing of Spent Fuel, 2005; ANS Annual Meeting; DOE/NE-SWG meeting, Albuquerque, NM Dec. 2010

Volatile Gases



Nanofiber Separations

Waste Form

Dry Chlorination

Fuel Assemblies

Hardware Removal & Decladding

Used Bare Fuel

Volox, Chlorination, or Fluorination

Fresh Fuel

Used Oxide Fuel

Fuel Fab

MOX Fuel Assemblies

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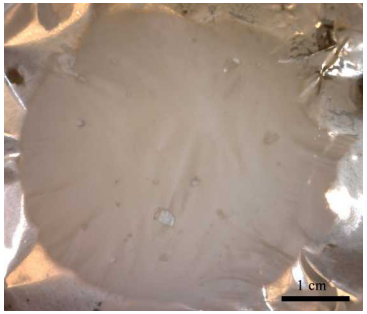
Off Gas Separations Membranes for MOC Fuel Cycle Applications

High Temperature Volatile Gas Capture Materials

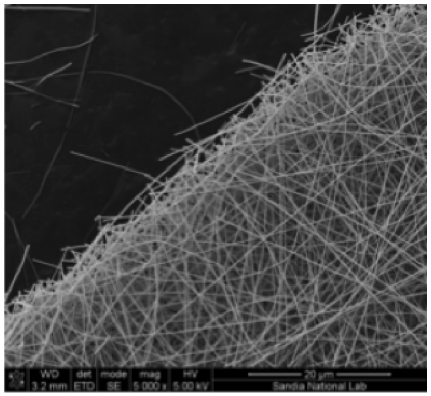
Nanofiber Membranes:

- **High flux** (accessibility to high open surface area)
- **Easy Insertion in off-gas streams** (membrane)
- **Compatible with innovative separation technologies**
- **Chemical, mechanical, radioactive durability**
- **High capacity** (high waste loading)
- **Selectivity** (catch trace amount of residue)
- **Functionalization:** Bulk Surface and Internal Pore System

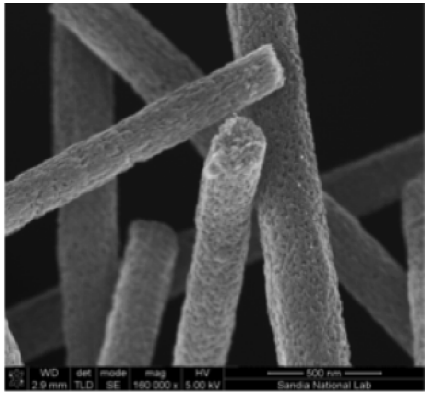
To Date:



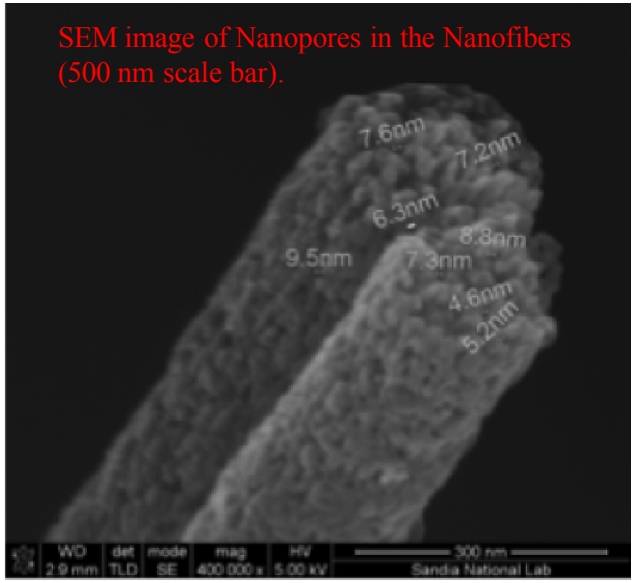
Optical image of membrane



SEM image of Nanofiber Membrane (20 micron scale bar)



SEM image of Nanofibers (500 nm scale bar)



Conclusions

- Understanding the fundamentals to better design the capture material and waste form
- The Capture Material and the Waste Form can be designed for each other to ensure materials compatibility and processing simplicity
- Understanding of Waste Form performance criteria will greatly aid in design and implementation

Acknowledgements

- Sandia National Laboratories is a multi-program lab managed and operated by Sandia Corp., a wholly owned subsidiary of Lockheed Martin Corporation, for the US DOE's NNSA under contract DE-AC04-94AL85000.
- Continued financial support from DOE/NE-FCRD-SWG